Comparative Study of Thermally Conductive Fillers for Use in Liquid Encapsulants for Electronic Packaging

C. P. Wong, *Fellow, IEEE,* and Raja S. Bollampally

***Abstract*—Thermal management plays a very vital role in the packaging of high performance electronic devices. Effective heat dissipation is crucial to enhance the performance and reliability of the packaged devices. Liquid encapsulants used for glob top, potting, and underfilling applications can strongly influence the package heat dissipation. Unlike molding compounds, the filler loading in these encapsulants is restrained. This paper deals with the development and characterization of thermally conductive encapsulants with relatively low filler loading. A comparative study on the effect of different ceramic fillers on the thermal conductivity and other critical properties of an epoxy based liquid encapsulant is presented.**

***Index Terms*—Composites, encapsulants, packaging, polymer, thermal conductivity.**

I. Introduction

TRADITIONALLY, epoxy based encapsulants are filled with silica, that has a relatively low thermal conductivity of 1.5 W/mK. As semiconductor devices increase in transistor densities, the heat dissipation requirements increase, resulting in the need for improved thermally conducting packaging materials [1]. The use of thermally conductive encapsulants enhances the thermal performance of packages that are small and have modest heat dissipation requirements. In flip chip assemblies the gap between the chip and the board is very small (<4 mils). As a result, the thermal resistance of the underfill material that fills in this gap is very small when compared to the overall resistance. Thus, marginal improvement in the thermal conductivity of the underfill might not contribute much to decreasing the overall resistance. But in the case of glob top coatings, and potting compounds, a marginal increase in the thermal conductivity could result in a substantial improvement in the thermal performance of the package. The technical challenge is to develop encapsulants with improved thermal conductivity without compromising on other key properties like coefficient of thermal expansion (CTE), modulus, viscosity and moisture absorption.

The use of ceramic fillers to enhance the thermal conductivity of epoxy molding compounds has been studied extensively [2]–[5]. The filler loading in these encapsulants is high (up to 90 wt%). For liquid encapsulants like glob top coatings, potting compounds, and underfill materials used in flip chip on board (FCOB), the filler loading is generally lower than 75 wt%. This is to facilitate the process of dispensing the encapsulant with ease. Our study focuses on the use of ceramic fillers within this region of low filler loading. Ceramic fillers like boron nitride, alumina, and aluminum nitride coated with silica are used in this study and their performance is compared with silica filled samples. A detailed study on the effect of these fillers at various loading ratios on the thermal conductivity, modulus, CTE, viscosity and moisture absorption is reported in this work. Also, the thermal conductivity of the filled composites, which is the main theme of this paper, was compared with well known models in literature.

Maxwell pioneered in the study of the thermal conductivity of two-phase mixtures [6]. Using potential theory, he obtained a relationship for the conductivity of a two phase mixture consisting of randomly distributed and noninteracting homogenous spheres in a homogenous medium

$$k_c = k_m \frac{k_p + 2k_m + 2\phi(k_p - k_m)}{k_p + 2k_m - \phi(k_p - k_m)} \tag{1}$$

where k_c, k_m, and k_p are the thermal conductivities of the composite, matrix, and the particles (filler), respectively and ϕ is the volume fraction of the filler. This model predicts the thermal conductivity of composites fairly well for low filler concentrations and is not valid at high concentrations when the filler particles begin to touch each other.

Bruggeman [7] developed an implicit relationship between the thermal conductivities of the composite, the filler, and the matrix for dilute suspension of spheres

$$1 - \phi - \left(\frac{k_p - k_c}{k_p - k_m}\right)\left(\frac{k_m}{k_c}\right)^{1/3}. \tag{2}$$

Agari and Uno [8] developed a new model based on the generalization of models for series and parallel conduction in composites

$$k_c = \left[\frac{k_p^{C_2}}{C_1 k_m}\right]^{\phi} (C_1 k_m) \tag{3}$$

which can be rearranged as

$$\log k_c = \phi C_2 \log k_p + (1 - \phi)\log(C_1 k_m) \tag{4}$$

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TABLE I
CHARACTERISTIC PROPERTIES OF THE FILLERS

Filler	Silica	BN	SCAN	Alumina
Density (gm/cc)	2.2	2.25	3.26	3.98
Thermal Conductivity (W/mK)	1.5	250-300	160-260	36
CTE (PPM/°C)	0.5	<0.5	4.4	6.6
Young's Modulus (Gpa)	73	43	330	385

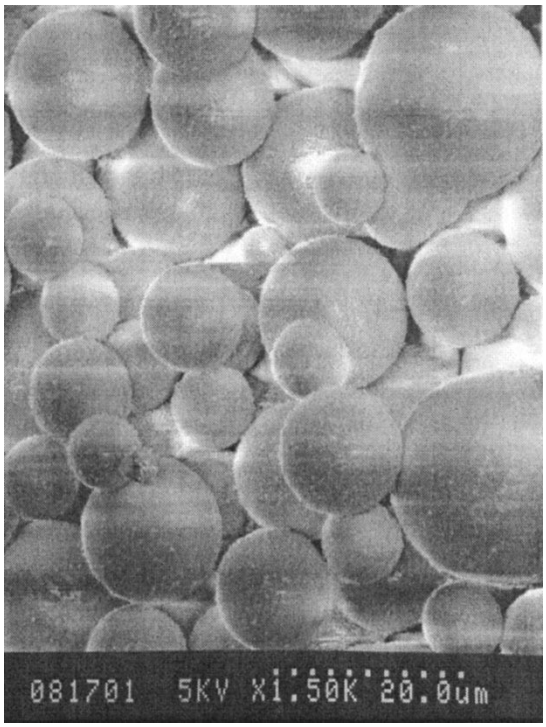

Fig. 1. SEM micrograph of silica.

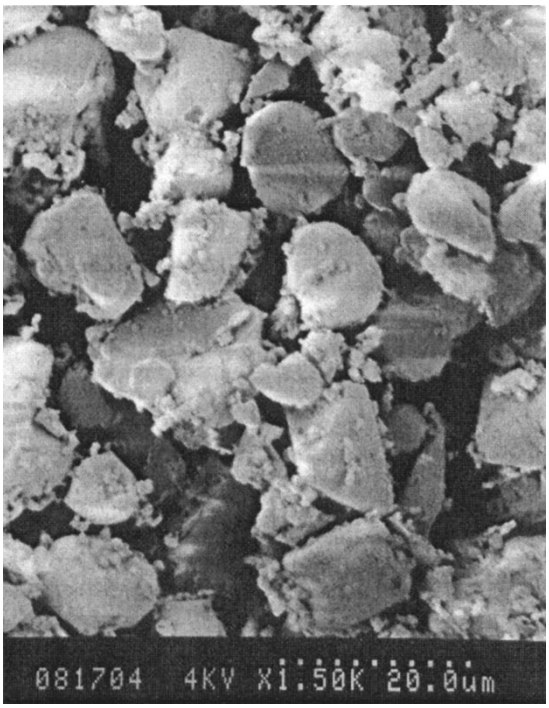

Fig. 2. SEM micrograph of alumina.

where, C_1 and C_2 are experimentally determined constants. C_1 is a measure of the effect of particles on the secondary structure of the polymer and C_2 is a measure of ease with which the particles begin to form conductive chains.

II. EXPERIMENTAL

A. Materials

The epoxy resin used for the study was 3,4-epoxy cyclohexyl methly-3,4-epoxy cyclohexyl caboxylate, manufactured by Union Carbide. The hardener used was hexahydro-4-methlypthalic anhydride from Aldrich Chemical Company. The catalyst used for curing was Iron (III) acetyl acetonate also from Aldrich Chemical Company. All the above chemicals were used as received. The above system was chosen because of its low viscosity. The fillers used were boron nitride (BN) from Advanced Ceramics Corporation, silica coated aluminum nitride (SCAN) from Dow Chemical Company, alumina from Showa Denko, and silica from Nippon Chemicals. Surface treated BN was received directly from the vendor, whereas a titanate coupling agent, tetra (2,2 diallyoxymethyl) butyl di (ditridecyl) phosphito titanate, from Kenrich Petrochemicals, was used to treat the silica and alumina surfaces. All the fillers had an average particle size of 12-15 μm. Boron Nitride was platelet shaped, SCAN was irregular, alumina was close to spherical and silica had a perfect spherical shape. Figs. 1–4 are typical SEM micrographs of silica, alumina, SCAN and BN, respectively. Table I shows the important characteristics of the fillers used.

B. Sample Preparation

The epoxy resin and hardener were mixed thoroughly in a ratio of 1 : 1 (by weight) before the catalyst was added. This mixture was then stirred for about 3 h until the catalyst was fully dispersed. The titanate coupling agent was then added to the mixture. The amount of titanate used was 1% by weight of the filler. A Waring commercial blender was used to mix the filler with the above resin/hardener mixture. After mixing, the samples were placed in a vacuum oven for about 1 h to

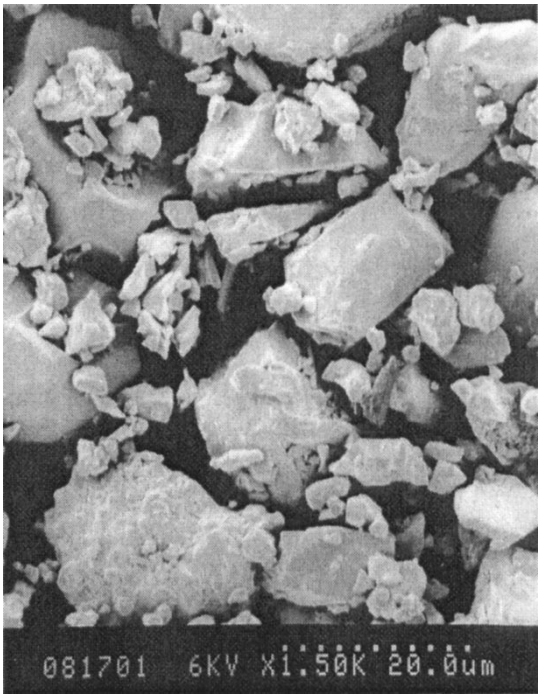

Fig. 3. SEM micrograph of SCAN.

Fig. 4. SEM micrograph of BN.

remove the entrapped air in the samples. These formulations were stored in a freezer at −40 °C when not in use.

C. Measurement Methods

1) Thermal conductivity: The thermal conductivity measurements were made on a Holometrix TCA-200 guarded heat flow meter. These tests comply with ASTM F433, E1530 standard methods for determining the thermal conductivity. Vespel, Pyrex, and Pyroceram were used as the standards in the calibration of the instrument. A thermally conductive heat sink compound was used to minimize the contact resistance between the sample and the hot/cold plates of the instrument. The maximum temperature gradient across the sample during measurement was 75 °C. The samples used were made by curing the filled epoxy formulations in 1.5-in diameter aluminum pans. These pans were placed in a convective oven and heated to 250 °C at a rate of 3 °C/min. The samples were held at this temperature for another 15 min. The cured samples were then cooled down to room temperature and machined into squares having dimensions of 1" × 1." The thickness of the samples ranged from 0.1–0.2." The machined samples were used for thermal conductivity measurements. Upon reaching thermal equilibrium, output data from the test are read on a digital display and thermal conductivity values are then computed using a utility software program. The conductivity was measured at a mean sample temperature of 70 °C. The reported values are the averages of two measurements per sample.

2) Coefficient of thermal expansion (CTE): CTE measurements of the cured samples were performed on a Thermal Mechanical Analyzer (TMA) (TA Instruments, Model 2940). These samples were prepared in a similar way as the samples for thermal conductivity measurement except that the samples were much smaller in size (4 × 4 × 2 mm). The samples were mounted on the TMA and heated to 250 °C at a heating rate of 10 °C/min. The coefficient of thermal expansion was determined from the slope of the thermal expansion versus temperature plot. The CTE was measured for two different samples with the same composition and the average value is reported.

3) Storage modulus: A dynamic mechanical analyzer (DMA) (TA Instruments, Model 2980) was used to determine the storage moduli of the samples. The samples for DMA tests were made in the same way as those for TMA tests except that these samples were in the form of strips having dimensions of about 32 × 11 × 3 mm. A single cantilever mode under 1 Hz sinusoidal strain loading was used for the tests. The specimen was mounted on the DMA and heated from room temperature to 300 °C at a heating rate of 3 °C/min. The storage modulus (E') was calculated using a preinstalled software program. The data reported is the modulus at 25 °C and is the average of measurements on two different samples with the same composition.

4) Viscosity: The viscosity of the formulations was measured using a controlled stress rheometer (TA Instruments, Model AR1000-N). Parallel plate geometry was used and the shear rate ranged from 0.1–20/s. All the measurements were made at 25 °C and the samples used were uncured.

5) Adhesion strength: Adhesion strength of the epoxy to silica and alumina interfaces was accomplished in a shear mode using a bond tester (Model 550-100K, Royce Instruments). To test the adhesion between the resin and silica interface, 80 × 80 mil SiO_2 passivated silicon die were used. A thin layer of the epoxy resin was applied to the die and these were then placed on a SiO_2 passivated silicon substrate. The epoxy resin was then cured under the same conditions as

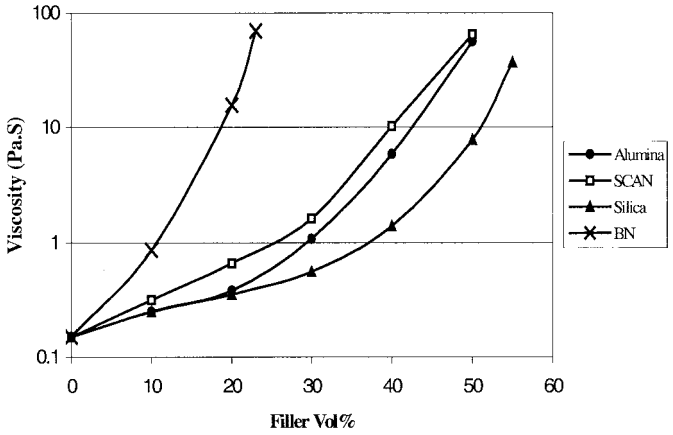

Fig. 5. Viscosity as a function of filler loading.

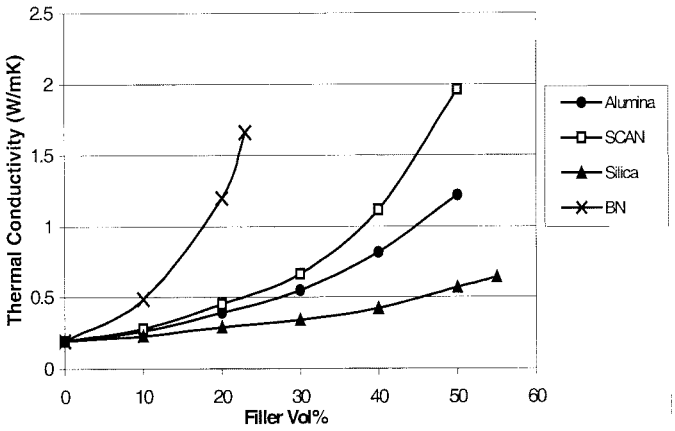

Fig. 6. Thermal conductivity as a function of filler loading.

specified earlier. For measuring the adhesion strength between the resin and alumina interface, similar die (80 × 80 mil SiO_2 passivated silicon) were used on a alumina substrate. In either case, adhesion measurements were done on 20 die and the average strength was obtained.

6) Moisture absorption: The cured samples were placed in a humidity chamber (BLUE M, Model AC-7602HA-1) at 85 RH/85 °C. These samples were initially weighed before placing in the humidity chamber and their weight was subsequently recorded after fixed intervals of time. The data was recorded for a period of 1000 h and the percent weight gain was determined with respect to time.

III. Results and Discussion

In the results presented below, the filler loading is always expressed in volume percent unless stated otherwise. The following relation was used to determine the volume fraction of the filler for a given weight fraction

$$\phi = \frac{W}{W + (1 - W)\dfrac{\rho_f}{\rho_m}} \tag{5}$$

where ϕ is the volume fraction, W is the weight fraction, ρ_f is the density of the filler and ρ_m is the density of the matrix.

A. Material Characterization

1) Viscosity as a function of filler loading: All the filled samples showed slight shear thinning or shear thickening at lower shear rates. The viscosities reported here are at a temperature of 25 °C and a shear rate of 5/s. With all the fillers, viscosity increases with filler loading as can be seen from Fig. 5. BN filled samples have the highest viscosity for any given filler loading, while silica filled ones have the lowest viscosity. The spherical shape of silica is responsible for the low viscosity of silica filled samples. BN has a platelet like shape that results in high viscosity of samples filled with it. This limits the maximum filler loading to 23% for BN. The viscosity of SCAN and alumina filled samples were in between those for silica and BN. Also, alumina was close to spherical and results in lower viscosity than SCAN which had an irregular shape. It is thus clear from the above study that the shape of the filler plays a very important role in determining the viscosity of filled resins. A resin filled with spherical particles has a lower viscosity than those with nonspherical particles. Similar results were reported by M. Ko *et al.* [9], who studied the effect of particle shape on silica filled epoxy molding compounds. At 50% loading, SCAN and alumina filled samples have a viscosity that is below 70 Pa·s which is desirable for liquid encapsulants.

2) Thermal conductivity as a function of filler loading: The thermal conductivity as a function of filler loading is shown in Fig. 6. It shows a super-linear increase with increase in the filler loading (the slope of the curve increases with increase in filler loading). For any given filler loading, BN filled samples have the highest conductivity while silica filled formulations have the lowest conductivity. The nonspherical (platelet) shape of BN results in a better contact between the particles which is responsible for the higher thermal conductivity of these samples when compared to other filled systems. For given volume, a sphere has the least surface area and the surface area increases with increase in the aspect ratio (nonsphericity). Thus, platelets result in better inter-particulate contact than spheres at the same volume loading. The low conductivity of silica filled formulations is due to the low thermal conductivity of fused silica (1.5 W/mK). A conductivity of about 2 W/mK was achieved with 50% SCAN. This is about 10 times the intrinsic conductivity of the polymer. Though, the thermal conductivity of the filled composites is higher than that of the resin, it is a few orders of magnitude lower than that of the intrinsic conductivity of the fillers. This is because the low thermal conductivity of the resin acts as a barrier for heat conduction between the filler particles that are dispersed in the polymer matrix. Figs. 7–10 show the comparison between theoretical models and experimental data for the thermal conductivity of silica, alumina, SCAN and BN filled systems. For silica filled systems, both Maxwell model and Agari and Uno model provide a better estimate of thermal conductivity compared to the Bruggeman model. For alumina SCAN, and BN filled systems, Agari, and Uno model fits the data fairly well. The constants C_1 and C_2 in the Agari and Uno model are determined by curve fitting of the experimental data and hence, this model represents the data better than other models.

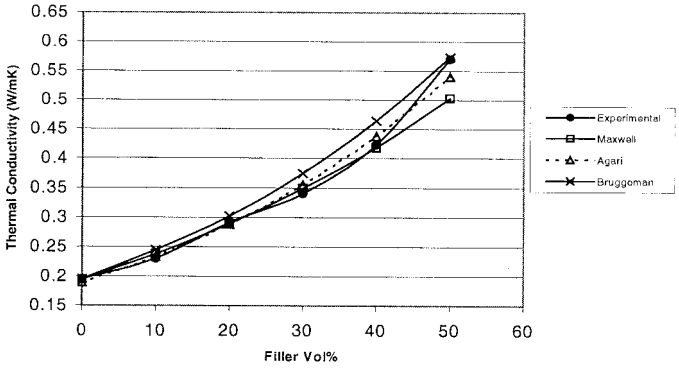

Fig. 7. Comparison of thermal conductivity of silica filled composites with theoretical predictions.

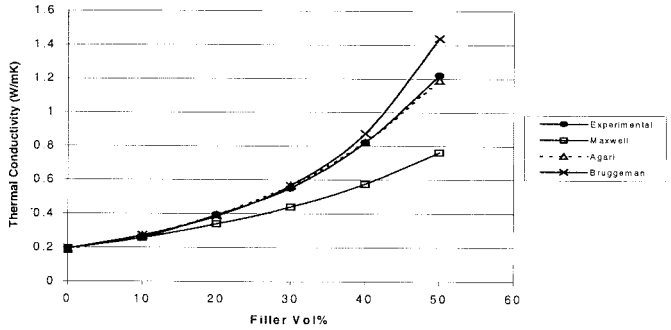

Fig. 8. Comparison of thermal conductivity of silica filled composites with theoretical predictions.

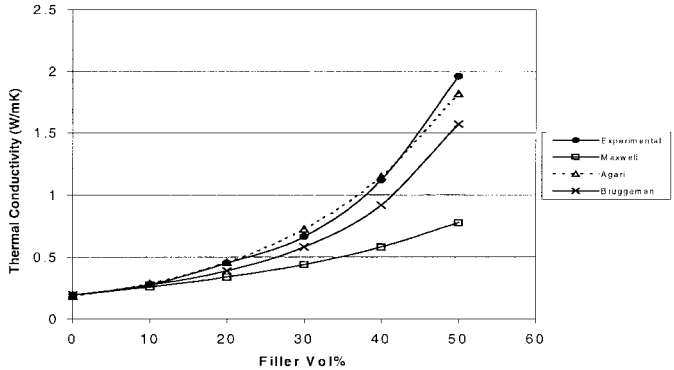

Fig. 9. Comparison of thermal conductivity of SCAN filled composites with theoretical predictions.

3) CTE as a function of filler loading: The CTE before T_g of the cured resin without any filler is about 88 ppm/°C. From Fig. 11 it can be seen that with increase in the filler content, the CTE decreases. For any given filler loading, BN filled samples have the lowest CTE and alumina filled samples have the highest CTE. This can be explained as follows. The intrinsic CTE's of the fillers in the order of increasing magnitude is BN<silica<SCAN<alumina. Therefore, for any given filler loading, the composite CTE's follow the same order as that of the fillers.

4) Storage modulus as a function of filler loading: Fig. 12 shows the plot of storage modulus as a function of filler loading for different fillers. The increase in the modulus with filler loading shows the same super linear trend as observed

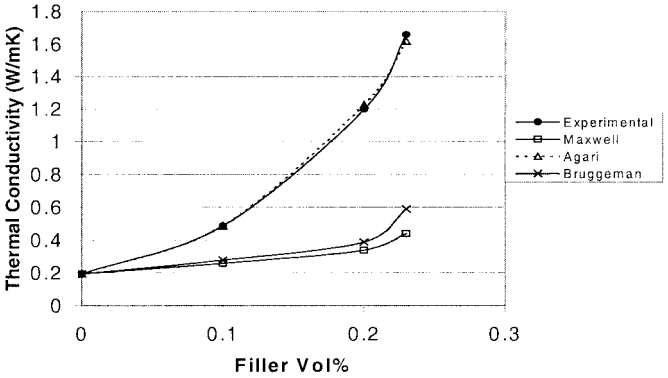

Fig. 10. Comparison of thermal conductivity of BN filled composites with theoretical predictions.

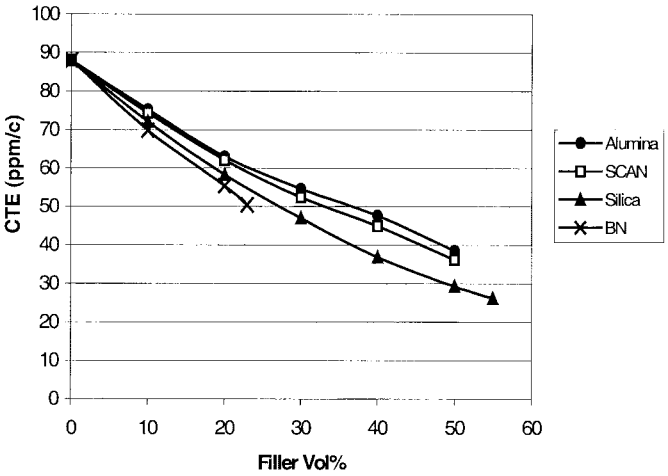

Fig. 11. CTE as a function of filler loading.

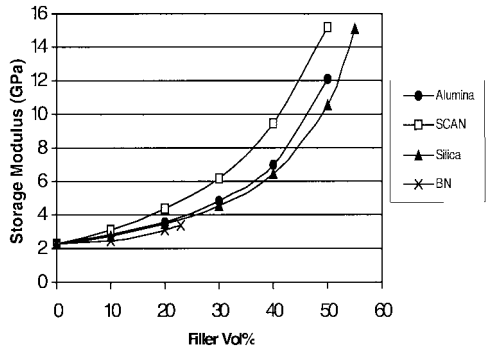

Fig. 12. Storage modulus as a function of filler loading.

with thermal conductivity. For any given filler loading, SCAN filled samples have the highest modulus. Although, the intrinsic modulus of alumina is the highest of all the fillers, alumina filled samples do not have higher moduli than those with SCAN. This can be attributed to the greater degree of irregularity in the shape of SCAN particles when compared to alumina. These results confirm the theoretical predictions of Wu [10]. Another possible reason to explain the higher modulus of SCAN filled composites is better adhesion between the silica interface of SCAN and epoxy than the adhesion between alumina interface and epoxy. Interfacial adhesion between silica and alumina surfaces with epoxy was studied

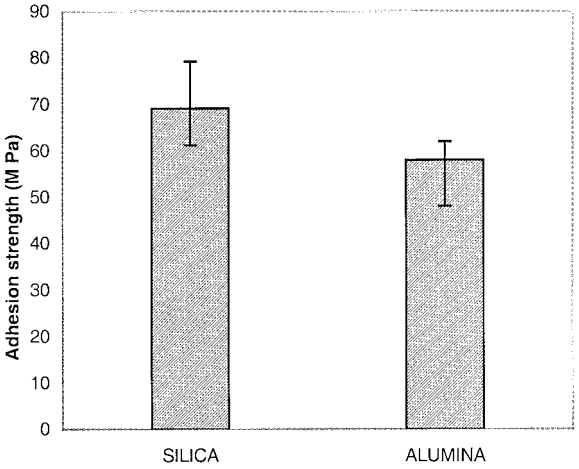

Fig. 13. Adhesion strength between the silica and alumina interfaces with the epoxy resin.

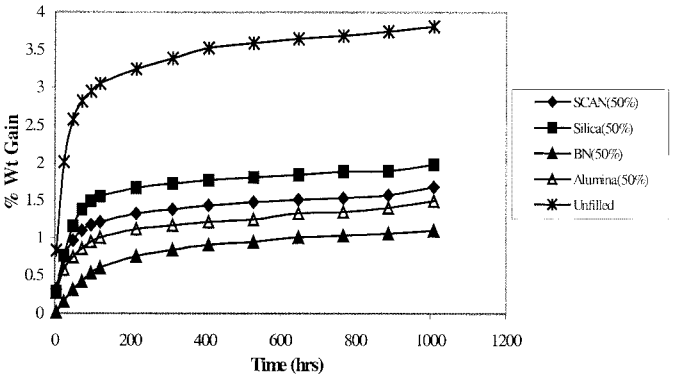

Fig. 14. Moisture absorption as a function of time.

in order to justify the explanation. Fig. 13 shows the results of the adhesion strength of epoxy to silica and alumina interfaces as determined from the die shear measurements. It can be seen that the adhesion strength between epoxy and silica interface is higher than that between epoxy and alumina interface. Good interfacial adhesion between the resin and the filler results in better reinforcement and hence a higher modulus.

5) Moisture absorption: Fig. 14 shows the percent weight gain as a function of time for samples with different fillers. The filler loading was 50% (by weight) for all the samples. It can be seen that BN filled samples have the lowest moisture uptake. Silica filled samples have higher weight gain compared to those filled with SCAN which in turn have higher moisture uptake than those filled alumina. The unfilled epoxy has a much higher moisture uptake than any of the filled samples. The comparatively high moisture absorption of silica filled samples is due to the presence of silanol (Si-OH) groups that have a tendency to absorb moisture by forming hydrogen bonds with water.

IV. Conclusion

It can be seen that the thermal conductivity of alumina, SCAN, and BN filled composites is much higher than those filled silica. SCAN filled samples have key properties desirable for liquid encapsulants. At a loading of 50%, the thermal conductivity of SCAN filled composites is ten times the intrinsic thermal conductivity of the epoxy resin. Also, it was found that the Agari and Uno model fits the thermal conductivity data fairly well. The study on the modulus of elasticity showed that adhesion between the resin and filler plays an important role in determining the composite modulus. SCAN filled composites have the highest modulus for any given filler loading. Silica filled composites have the lowest CTE at any given filler loading and also have the highest moisture uptake.

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C. P. Wong (SM'87–F'92), for a photograph and biography, see this issue, p. 53.

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